

Fisher Waves in the Diffusion-Limited Coalescence Process $A + A \rightleftharpoons A$

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Fisher waves have been studied recently in the specific case of diffusion-limited reversible coalescence, $A + A \rightleftharpoons A$, on the line. An exact analysis of the particles concentration showed that waves propagate from a stable region to an unstable region at constant speed, just as in Fisher's "mean-field" theory; but also that the wave front fails to retain its initial shape and instead it broadens with time. Our present analysis encompasses the full hierarchy of multiple-point density correlation functions, and thus it provides a complete exact description of the same system. We find that as the wave propagates, the particles in the stable phase remain distributed exactly as in their initial (equilibrium) state. On the other hand, the leading particle—the one at the edge of the wave—advances as a biased random walk, rather than simply linearly with time. Thus the shape of the wave remains actually constant, but it is the "noisy" propagation of the wave's edge that causes its apparent broadening.

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Fisher waves [1,2] are the best known paradigm of the invasion of an unstable phase by a stable phase. Fisher's theory describes the kinetics of particles concentration $\rho(x_1, x_2, \dots, x_d, t)$ in a reaction process (taking place in d -dimensions) at the level of a reaction-diffusion equation [1,2]:

$$\frac{\partial \rho}{\partial t} = D \Delta \rho + k_1 \rho - k_2 \rho^2. \quad (1)$$

Here D is the effective diffusion constant of the particles, and k_1 and k_2 are rates of particle generation and particle death, respectively. Eq. (1) admits two stationary solutions:

$$\rho = 0, \quad (2)$$

and

$$\rho = k_1/k_2, \quad (3)$$

but only the latter is stable. Suppose that the system is prepared at the initial state: $\rho = k_1/k_2$ for $x_1 \leq 0$, and $\rho = 0$ for $x_1 > 0$. Then the stable phase ($\rho = k_1/k_2$) invades the unstable phase ($\rho = 0$) in the form of a wave, $\rho(x_1, \dots, x_d, t) = f(x_1 - ct)$, which travels unchanged at constant speed $c \geq c_{\min} = 2\sqrt{k_1 D}$. The minimal speed is realized for sufficiently sharp initial interfaces [3] (such as in our case).

Fisher's equation might be regarded as a "mean-field" approximation to the kinetics of diffusion-limited coalescence, $A + A \rightleftharpoons A$: The reaction terms of Eq. (1) are in the form of the mass action rate equation appropriate for systems in local equilibrium, as might be expected for reaction-limited kinetics. Recently, however, diffusion-limited reversible coalescence was analyzed *exactly* in one

dimension [4]. It was found that, just as in the Fisher theory, waves propagate at a constant speed from a stable to an unstable phase, but that the width of the wave front broadens with time as $w \sim \sqrt{t}$. The broadening of the wave front is of special interest since it represents the effects of the internal noise in the system—the noise which Fisher's equation fails to model.

In ref [4] exact expressions were derived for the particle *concentration*, following the method of Inter-Particle Distribution Functions (IPDF). In this letter, we exploit the same method to derive the *full distribution* of particles, as represented by the infinite hierarchy of n -point density correlation functions. (The particle concentration corresponds to the special case of $n = 1$.) We find that as the wave propagates, the particles in the stable phase remain distributed exactly as in their initial (equilibrium) state. On the other hand, the leading particle—the one at the edge of the wave—advances as a biased random walk, rather than simply linearly with time. In this view, the shape of the wave remains actually constant in any particular realization of the process. The apparent broadening is the result of the fluctuations in the location of the wave's edge among different realizations (Fig. 1).

The coalescence model [4–7] is defined on a one-dimensional lattice of lattice spacing a . Each site is in one of two states: occupied by a particle A , or empty. Particles hop randomly into nearest neighbor sites, at rate D/a^2 . A particle may give birth to an additional particle, into a nearest neighbor site, at rate v/a (on either side of the particle) [8]. If hopping or birth occurs into a site which is already occupied, the target site remains occupied. The last rule means that coalescence, $A + A \rightarrow A$, takes place *immediately* upon encounter

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of any two particles. Thus, together with hopping and birth, the system models the diffusion-limited reaction process $A + A \rightleftharpoons A$. The system's dynamical rules are illustrated in Fig. 2.

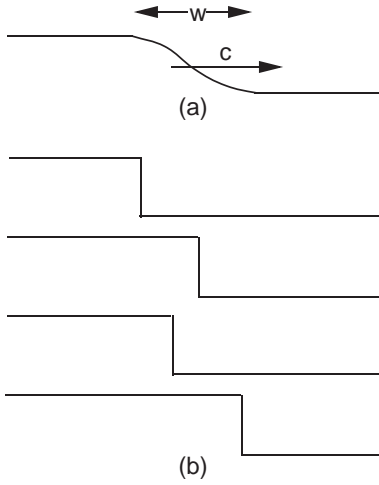


Figure 1. Fisher waves: (a) The ensemble average yields a wave traveling at speed $c = v$, with a front that broadens with time as $w \sim \sqrt{Dt}$. (b) Individual waves actually remain sharp throughout the motion, but their fronts travel in an erratic fashion, leading to the ensemble average in (a). Fisher's classical theory predicts a wave as in (a), but its front does not broaden with time.

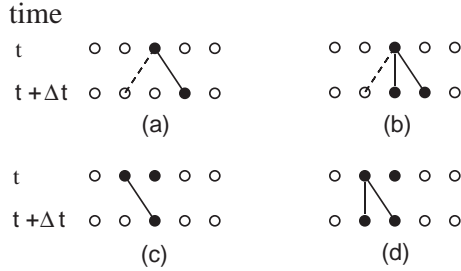


Figure 2. Reaction rules: (a) diffusion; (b) birth; and coalescence, (c) following diffusion, and (d) following a birth event. The dotted lines in (a) and (b) indicate alternative target sites.

The IPDF method used for the exact analysis relies on the key concept of $E_{n,m}(t)$ —the probability that sites $n, n+1, \dots, m$ are empty at time t . The probability that site n is occupied is

$$\text{Prob}(\text{site } n \text{ is occupied}) = 1 - E_{n,n} . \quad (4)$$

The event that sites n through m are empty (prob. $E_{n,m}$) consists of two cases: site $m+1$ is also empty (prob. $E_{n,m+1}$), or it is occupied. Thus the probability that sites n through m are empty, but site $m+1$ is occupied is $E_{n,m} - E_{n,m+1}$. With this (and with a similar rule for when the particle is to the left of the empty segment) one can write down a rate equation for the evolution of the empty interval probabilities [4–7]:

$$\begin{aligned} \frac{\partial E_{n,m}}{\partial t} = & \frac{D}{a^2}(E_{n,m-1} - E_{n,m}) \\ & - \frac{D}{a^2}(E_{n,m} - E_{n,m+1}) \\ & - \frac{D}{a^2}(E_{n,m} - E_{n-1,m}) \\ & + \frac{D}{a^2}(E_{n+1,m} - E_{n,m}) \\ & - \frac{v}{a}[(E_{n,m} - E_{n,m+1}) + (E_{n,m} - E_{n-1,m})] . \end{aligned} \quad (5)$$

For example, the first term on the r.h.s. represents the event that sites $n, \dots, m-1$ are empty and a particle at site m hops to $m+1$, thus increasing $E_{n,m}$. The second term represents the decrease in $E_{n,m}$ when a particle at $m+1$ hops into the empty interval n, \dots, m , etc. Eq. (5) is valid for $m > n$. The special case of $m = n$ yields the boundary condition

$$E_{n,n-1} = 1 . \quad (6)$$

The fact that the $\{E_{n,m}\}$ represent *probabilities* implies the additional condition that $E_{n,m} \geq 0$. Finally, if the system is not empty then $E_{n,m} \rightarrow 0$ as $n \rightarrow -\infty$ and $m \rightarrow \infty$.

Rather than working with the discrete equations, it is simpler to pass to the continuum limit. We write $x = na$ and $y = ma$, and replace $E_{n,m}(t)$ with $E(x, y, t)$. Letting $a \rightarrow 0$, Eq. (5) becomes

$$\frac{\partial E}{\partial t} = D\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2}\right)E - v\left(\frac{\partial E}{\partial x} - \frac{\partial E}{\partial y}\right) , \quad (7)$$

with the boundary conditions,

$$E(x, x, t) = 1 , \quad (8)$$

$$E(x, y, t) \geq 0 , \quad (9)$$

$$\lim_{\substack{x \rightarrow -\infty \\ y \rightarrow +\infty}} E(x, y, t) = 0 . \quad (10)$$

The concentration of particles is obtained using Eqs. (4) and (6), and passing to the continuum limit:

$$\rho(x, t) = -\frac{\partial E(x, y, t)}{\partial y} \Big|_{y=x} . \quad (11)$$

It can also be shown [4,9] that the conditional joint probability for having particles at x and y but none in between, is

$$P_2(x, y, t) = -\frac{\partial^2 E(x, y, t)}{\partial x \partial y} . \quad (12)$$

Given a particle at x , the probability that the next nearest particle to its *right* is at y , i.e., the “forward” IPDF, is

$$p(x, y, t) = \rho(x, t)^{-1} P_2(x, y, t) . \quad (13)$$

Likewise, the “backward” IPD, the probability that the next nearest particle to the *left* of a given particle at y is at x , is

$$q(x, y, t) = \rho(x, t)^{-1} P_2(x, y, t) . \quad (14)$$

Eq. (7) admits two homogeneous stationary solutions:

$$E(x, y) = 1 , \quad (15)$$

and

$$E_{\text{eq}}(x, y) = e^{-\frac{v}{D}(y-x)} . \quad (16)$$

The first solution implies $\rho = 0$, while the second solution describes active *equilibrium*, with

$$\rho_{\text{eq}} = v/D \equiv \gamma . \quad (17)$$

These states correspond, respectively, to the unstable and stable phases of Fisher’s theory (Eqs. 2 and 3). It is important to notice that in the equilibrium phase the particles are distributed independently from each other. Indeed, suppose that the particles are so distributed, at a homogeneous concentration γ . Then, the probability that there are no particles in an infinitesimal interval of length $\Delta\xi$, is $(1 - \gamma\Delta\xi)$. Since in equilibrium the particles are uncorrelated, the probability that a finite interval of length $\xi = y - x$ is empty, is $(1 - \gamma\Delta\xi)^{\xi/\Delta\xi}$. The equilibrium empty interval probability is then recovered by taking the limit $\Delta\xi \rightarrow 0$. Notice also that in the equilibrium state the IPDF (both forward or backward) is

$$p_{\text{eq}}(x, y, t) = q_{\text{eq}}(x, y, t) = \gamma e^{-\gamma(y-x)} . \quad (18)$$

This can be derived from Eqs. (12)–(14), and (16), as well as from the properties of uncorrelated, randomly distributed particles.

Suppose now that a system is prepared in the following initial state: at $x < 0$ the particles are distributed as in the equilibrium distribution, Eq. (16), and at $x > 0$ there are no particles (the unstable steady state). The initial concentration profile is then

$$\rho(x, 0) = \frac{v}{D} [1 - H(x)] = \begin{cases} v/D, & x < 0 \\ 0, & x > 0 \end{cases} \quad (19)$$

where $H(\cdot)$ is the Heavyside step function. Doering et al. [4] have shown that in this case the concentration profile evolves as

$$\rho(x, t) = \frac{v}{2D} \text{erfc}\left(\frac{x - vt}{\sqrt{4Dt}}\right) , \quad (20)$$

where $\text{erfc}(\cdot) = 1 - \text{erf}(\cdot)$ is the complementary error function [10]. That is, the initial step-wave propagates at speed v , while at the same time the wave front broadens as $w \sim \sqrt{Dt}$.

Doering et al. [4] have also considered the same initial condition as above, but when a particle is known for sure to be at the front’s edge at $x = 0$:

$$\rho(x, 0) = \frac{v}{D} [1 - H(x)] + \delta(x) . \quad (21)$$

In this case the wave front acquires an additional peak which propagates at the same speed and broadens in the same fashion as before:

$$\rho(x, t) = \frac{v}{2D} \text{erfc}\left(\frac{x - vt}{\sqrt{4Dt}}\right) + \frac{1}{\sqrt{4\pi Dt}} \exp\left[-\frac{(x - vt)^2}{4Dt}\right] . \quad (22)$$

We now show that the distribution of particles in the coalescence system follows a simple and beautiful pattern: The particles in the stable phase—which are initially distributed as in equilibrium (Eq. 16)—remain distributed in the same fashion throughout the lifetime of the wave. The noisiness of the system is manifested in the motion of the leading particle (the one at the wave’s edge): rather than moving at constant speed $c = v$, it performs a biased random walk with average drift velocity v . Thus, the broadening of the wave front is the result of averaging over the shifting positions of the leading particle in different realizations of the process (Fig. 1). For simplicity, we first show that such an interpretation is consistent with the exact solution of ref. [4], and we defer the complete proof until later.

Let the position z of the leading particle be given by the distribution probability density $p(z, t)$. Let the other particles—those to the left of the leading particle—remain distributed as in equilibrium *at all times*. The probability that the interval (x, y) is empty at time t depends upon the location of the interval endpoints, x and y , with respect to that of the leading particle, z :

$$E(x, y, t) = \begin{cases} 1, & z < x < y , \\ 0, & x < z < y , \\ e^{-\gamma(y-x)}, & x < y < z . \end{cases} \quad (23)$$

Hence, taking into account the distribution of z ,

$$\begin{aligned} E(x, y, t) &= \int_{-\infty}^x p(z, t) dz + e^{-\gamma(y-x)} \int_y^{\infty} p(z, t) dz \\ &= P(x, t) + e^{-\gamma(y-x)} [1 - P(y, t)] , \end{aligned} \quad (24)$$

where in the last equation we introduced the definition

$$P(z, t) \equiv \int_{-\infty}^z p(z', t) dz' . \quad (25)$$

In terms of p , the concentration of particles (Eq. 11) becomes

$$\rho(x, t) = p(x, t) + \gamma [1 - P(x, t)] . \quad (26)$$

Notice also that the forward IPDF is

$$p(x, y, t) = \gamma e^{-\gamma(y-x)} \frac{p(y, t) + \gamma [1 - P(y, t)]}{p(x, t) + \gamma [1 - P(x, t)]} , \quad (27)$$

while the backward IPDF remains exactly as in equilibrium (Eq. 18), consistent with the postulated distribution of particles.

It is straightforward to verify that the proposed form of $E(x, y, t)$, Eq. (24), satisfies the boundary conditions (8)–(10). Putting $E(x, y, t)$ in Eq.(7) we see that it is also satisfied, provided that

$$\frac{\partial}{\partial t}P(z, t) = D\frac{\partial^2}{\partial z^2}P(z, t) - v\frac{\partial}{\partial z}P(z, t). \quad (28)$$

From the definition of P , we have the boundary conditions:

$$\lim_{z \rightarrow -\infty} P(z, t) = 0, \quad (29)$$

$$\lim_{z \rightarrow \infty} P(z, t) = 1, \quad (30)$$

$$P(z, t) \geq 0. \quad (31)$$

Finally, if a particle is known for sure to be present initially at $x = 0$ (Eq. 21), that particle is clearly the leading particle, and $p(x, 0) = \delta(x)$. Thus,

$$P(z, 0) = H(z). \quad (32)$$

The solution to Eq. (28) which satisfies the boundary conditions (29)–(31) and the initial condition (32), is

$$P(z, t) = \frac{1}{2} + \frac{1}{2}\text{erf}\left(\frac{z - vt}{\sqrt{4Dt}}\right). \quad (33)$$

Thus, using Eq. (26), we recover the prediction of Doering et al., Eq. (22). The probability density function for the position of the leading particle is particularly simple:

$$p(x, t) = (4\pi Dt)^{-1/2} \exp[-(x - vt)^2/4Dt], \quad (34)$$

and identical to that of a Brownian particle characterized by the diffusion coefficient D and subject to a drift v . A moment's reflection shows why this is the case: The particle at the edge of the wave can step to the right or left with equal probabilities, at rate D/a^2 . This explains diffusion. The drift is a result of the birth mechanism. If the leading particle gives birth onto the site to its left, the edge does not move. However, if the particle gives birth onto the site to its right then the edge moves to the right (at rate v/a). Because of this left/right asymmetry the walk performed by the edge is biased. —What is surprising, is that the particles trailing the edge remain distributed, on average, exactly as in their initial equilibrium distribution!

Consider now the initial condition (19), where the leading particle is not necessarily at $z = 0$. Because the particles are distributed as in equilibrium, the leading particle is at $z < 0$ with probability $p(z, 0) = \gamma e^{\gamma z}$ (and at $z > 0$ with probability 0). This case may be regarded as a superposition of systems of the previous type, where the leading particle is initially surely at z . Indeed, the linear combination

$$\rho(x, t) = \int_{-\infty}^0 \gamma e^{\gamma z} \left\{ \frac{v}{2D} \text{erfc}\left(\frac{x - z - vt}{\sqrt{4Dt}}\right) + \frac{1}{\sqrt{4\pi Dt}} \exp\left[-\frac{(x - z - vt)^2}{4Dt}\right] \right\} dz, \quad (35)$$

reproduces the known result of Eq. (20).

Up to this point we have merely found a distribution of particles which happens to explain the known results for E and for the concentration of particles ρ . It is conceivable, however, that other distributions might accomplish the same feat. A complete description of a particle system requires knowledge of the full hierarchy of n -point density-density correlation functions $\rho_n(x_1, x_2, \dots, x_n, t)$: the joint probability to find particles at x_1, x_2, \dots, x_n at time t . The particle concentration which was studied above corresponds to the special (limited) case of $n = 1$. The n -point correlation functions can too be analyzed exactly through the IPDF method [6]. We shall now describe the procedure and employ it for the conclusion of our proof.

Let $E_n(x_1, y_1, x_2, y_2, \dots, x_n, y_n, t)$ be the joint probability density that the intervals $[x_i, y_i]$ ($i = 1, 2, \dots, n$) are empty at time t . The intervals are non-overlapping, and ordered: $x_1 < y_1 < \dots < x_n < y_n$. Then, the n -point correlation function is given by

$$\rho_n(x_1, \dots, x_n, t) = (-1)^n \frac{\partial^n}{\partial y_1 \dots \partial y_n} E_n(x_1, y_1, \dots, x_n, y_n, t) \big|_{y_i = x_i}. \quad (36)$$

Doering [6] has shown that in our coalescence system the E_n satisfy the partial differential equation:

$$\begin{aligned} \frac{\partial}{\partial t} E_n(x_1, y_1, \dots, x_n, y_n, t) = \\ D \left(\frac{\partial^2}{\partial x_1^2} + \frac{\partial^2}{\partial y_1^2} + \dots + \frac{\partial^2}{\partial x_n^2} + \frac{\partial^2}{\partial y_n^2} \right) E_n \\ - v \left[\left(\frac{\partial}{\partial x_1} - \frac{\partial}{\partial y_1} \right) + \dots + \left(\frac{\partial}{\partial x_n} - \frac{\partial}{\partial y_n} \right) \right] E_n, \end{aligned} \quad (37)$$

with the boundary conditions

$$\begin{aligned} \lim_{x_i \uparrow y_i \text{ or } y_i \downarrow x_i} E_n(x_1, y_1, \dots, x_n, y_n, t) = \\ E_{n-1}(x_1, y_1, \dots, \cancel{x_i}, \cancel{y_i}, \dots, x_n, y_n, t), \end{aligned} \quad (38)$$

and

$$\begin{aligned} \lim_{y_i \uparrow x_{i+1} \text{ or } x_{i+1} \downarrow y_i} E_n(x_1, y_1, \dots, x_n, y_n, t) = \\ E_{n-1}(x_1, y_1, \dots, \cancel{y_i}, \cancel{x_{i+1}}, \dots, x_n, y_n, t), \end{aligned} \quad (39)$$

which should be obeyed for all $n > 1$. Here, we use the notation that crossed out arguments (e.g. $\cancel{x_i}$) have been removed. Notice how the E_n are tied together in an hierarchical fashion through the boundary conditions (38) and (39): one must know E_{n-1} in order to compute E_n . At the root of the hierarchy, $E_1 \equiv E$ is the simple empty interval probability that was studied above.

If our interpretation of the particles distribution is correct, then, following a reasoning similar to that which led to Eq. (24), we should have

$$\begin{aligned} E_n(x_1, y_1, \dots, x_n, y_n, t) &= P(x_1, t) \\ &+ e^{-\gamma(y_1 - x_1)} [P(x_2, t) - P(y_1, t)] \\ &+ \dots + e^{-\gamma\{(y_1 - x_1) + \dots + (y_i - x_i)\}} [P(x_{i+1}, t) - P(y_i, t)] \\ &+ \dots + e^{-\gamma\{(y_1 - x_1) + \dots + (y_n - x_n)\}} [1 - P(y_n, t)] . \end{aligned} \quad (40)$$

It is easy to confirm that these functions fulfill the boundary conditions (38) and (39). Eq. (37) is also satisfied, provided that P satisfies the same equation as before, Eq. (28). Using Eqs. (26), (36), and (40), we find the n -point correlation function:

$$\rho_n(x_1, \dots, x_n, t) = \gamma^{n-1} \rho(x_n, t) . \quad (41)$$

Thus, the joint probability density for finding particles at $x_1 < x_2 < \dots < x_n$ depends only on the rightmost particle at x_n —it alone is represented by the overall concentration profile. The particles at x_1, \dots, x_{n-1} are distributed randomly and independently of each other, with the equilibrium density γ . This is exactly what one would expect from the particle distribution that we have championed throughout this work, and it completes the proof to our claim.

In summary, we have shown that in one dimension the broadening of the wave front of Fisher waves in the coalescence system is truly due to the spread of locations of the leading particle in different realizations of the process. This peculiar situation, where the particles remain distributed as in the initial equilibrium configuration—and where all the changes are only reflected in the position of the leading particle—was recently found also in diffusion-limited coalescence in one dimension in the presence of a trap [9]. In fact, the proof in the present article may be carried over to that situation with only minor changes.

Fisher waves in the coalescence system have been studied numerically also in higher dimensions [11]. The goal there was to explore the effect of fluctuations intrinsic to particle systems as a function of dimensionality. The wave front was found to broaden as a power of time, with

an exponent which decreases with increasing d and becomes zero (as in Fisher's mean-field description) above the critical dimension of $d = 3$. The width of the wave front in ref. [11] was measured from the concentration profile, as averaged over an ensemble of different realizations. It would be interesting to repeat these simulations, but this time to subtract the fluctuations in the position of the wave front between different runs, as suggested from the present findings. This could result in a decrease of the width exponent, and possibly also in a decrease of the critical dimension for the validity of the mean-field Fisher picture.

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